

Validation of Data  
Nitroaromatics and Nitroamines by HPLC, SW-846, Method 8330A



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Annual Review

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## Scope and Applicability

This SOP offers detailed guidance in evaluating laboratory data generated according to "SW846-Method 8330A" January 1998. Method 8330A is used to determine the concentration of nitroaromatics and nitroamines organic compounds in extracts prepared from many types of solid waste matrices, soils, and water samples. The validation methods and actions discussed in this document are based on the requirements set forth in SW846 Method 8330A, Method 8000C and the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," January 2005. This document covers technical problems specific to each fraction and sample matrix; however, situations may arise where data limitations must be assessed based on the reviewer's professional judgement.

## Summary of Method

To ensure a thorough evaluation of each result in a data case, the reviewer must complete the checklist within this SOP, answering specific questions while performing the prescribed "ACTIONS" in each section. Qualifiers (or flags) are applied to questionable or unusable results as instructed. The data qualifiers discussed in this document are defined on page 4.

The reviewer must prepare a detailed data assessment to be submitted along with the completed SOP checklist. The Data Assessment must list all data qualifications, reasons for qualifications, instances of missing data and contract non-compliance.

## Reviewer Qualifications

Data reviewers must possess a working knowledge of SW846 Analytical Methods and National Functional Guidelines mentioned above.

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## DEFINITIONS

### Acronyms

CLP - Contract Laboratory Program  
CRQL - Contract Required Quantitation Limit  
%D - percent difference  
DoC - Date of Collection  
GC - gas chromatography  
HPLC - high performance liquid chromatography  
IS - internal standard  
kg - kilogram  
µg - microgram  
MS - matrix spike  
MSD - matrix spike duplicate  
ℓ - liter  
ml - milliliter  
PE - performance evaluation  
PEM - Performance Evaluation Mixture  
QC - quality control  
RAS - Routine Analytical Services  
RIC - reconstructed ion chromatogram  
RPD - relative percent difference  
RRF - relative response factor  
RRF - average relative response factor (from initial calibration)  
RRT - relative retention time  
RSD - relative standard deviation  
RT - retention time  
RSCC - Regional Sample Control Center  
SDG - sample delivery group  
SMC - system monitoring compound  
SOP - standard operating procedure  
SOW - Statement of Work  
SVOA - semivolatile organic acid  
TCL - Target Compound List  
TIC - tentatively identified compound  
TOPO - Task Order Project Officer  
TPO - Technical Project Officer  
VOA - Volatile organic  
VTSR - Validated Time of Sample Receipt

### Data Qualifiers

U -The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J -The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N -The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ -The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ -The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R -The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

**LAB QUALIFIERS:**

- D - The positive value is the result of an analysis at a secondary dilution factor.
- B - The analyte is present in the associated method blank as well as in the sample. This qualifier has a different meaning when validating inorganic data.
- E - The concentration of this analyte exceeds the calibration range of the instrument.
- A - Indicates a Tentatively Identified Compound (TIC) is a suspected adol-condensation product.
- X,Y,Z- Laboratory defined flags. The data reviewer must change these qualifiers during validation so that the data user may understand their impact on the data.

## PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER: \_\_\_\_\_ SDG# \_\_\_\_\_  
LAB: \_\_\_\_\_ SITE: \_\_\_\_\_

### 1.0 Introduction

- 1.1 The attached Standard Operating Procedure (SOP) is applicable to nitro substituted aromatic and nitro substituted amines by High Performance Liquid Chromatography (HPLC) data. Its scope is not only to facilitate the data validation process of the data reported by the contracting laboratory, but also to ensure the data is being reviewed in a uniform manner.
- 1.2 This SOP is based upon the quality control assurance requirements specified in analytical SW 846 Method 8330A Revision 1, January 1998, and the National Function Guidelines, January 2005.

### 2.0 Responsibilities

- 2.1 The reviewer must be knowledgeable of the analytical method and its criteria.
- 2.2 The reviewer must complete and/or file the following:

Data Assessment Checklist - The data reviewer evaluates Each criterion carefully and checks if data is in compliance, non-compliance or not applicable.

Data Assessment Narrative - The data reviewer must present professional judgement, address areas of concern and comment on the validity of the overall data package. The reviewer must explain the reasons for rejecting and or qualifying the data.

Telephone Record Log - All phone conversations must be transcribed by the reviewer. Upon completion of the data review, the original telephone log is attached to the data assessment narrative.

3.0 Data Completeness and Deliverables

3.1 Has all the data been submitted in CLP deliverable format?

3.2 Have any missing deliverables been received and added to the data package?

ACTION: Call lab for explanation/resubmittal of any missing deliverables. If lab cannot provide them, note the effect on review of the data in the reviewer narrative.

4.0 Cover Letter, SDG Narrative

4.1 Is a laboratory narrative or cover letter present?

4.2 Are the case number and/or SDG number contained in the narrative or cover letter?

5.0 Data Validation Checklist

5.1 Does this data package contain:

Water data?

Waste data?

Soil/solid data?

6.0 Traffic Reports and Laboratory Narrative

6.1 Are traffic report and chain-of-custody forms present for all samples?

ACTION: If no, contact lab for replacement of missing or illegible copies.

6.2 Do the traffic reports, chain-of-custody forms or SDG narrative indicate any problems with sample receipt, condition of the samples, analytical problems or



special circumstances affecting the quality of the data?

\_\_\_  \_\_\_

**ACTION:** If any sample analyzed as a soil, contains 50%-90% water, all data should be qualified as estimated, "J." If a soil sample contains more than 90% water, non detects shall be qualified as unusable, "R."

**ACTION:** If samples were not iced or if the ice was melted upon arrival at the laboratory and the temperature of the cooler was elevated ( $> 10^{\circ} \text{C}$ ), flag all positive results "J" and all non-detects "UJ".

## 7.0 Special QC

7.1 Prior to preparation of stock solutions; acetonitrile, methanol, and water should be analyzed to determine possible interferences with analyte peaks. A different batch of solvent should be used if contamination is present.

7.2 Chromatograms are to be submitted showing that there are no interferences with analyte peaks.

Are these chromatograms present in package?

\_\_\_ \_\_\_

Are the chromatograms free of interferences?

\_\_\_ \_\_\_

**Action:** Ask lab for resubmittals. If deliverables are unavailable, judge the effect of the validity of the data. If questionable, contact SMO and note in data assessment.

## 8.0 Holding Times

8.1 Have any nitroaromatics and nitroamines technical holding times, determined from date of collection to date of extraction, been exceeded?

\_\_\_  \_\_\_

Water and waste samples must be properly preserved (cooled to  $4^{\circ} \pm 2^{\circ}$ ), and nitro substituted aromatics and amines analysis must be extracted within 7 days of the date of collection. Extracts must be analyzed within 40 days of

the date of extraction. Soils and solid samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

**ACTION:** If technical holding times are exceeded, flag all positive results as estimated, "J," and sample quantitation limits "UJ" and document in the narrative that holding times were exceeded. If analyses were done more than 14 days beyond holding time, either on the first analysis or upon re-analysis, the reviewer must use professional judgement to determine the reliability of the data and the effects of additional storage on the sample results. At a minimum, all the data should at least be qualified "J", but the reviewer may determine that non-detects are unusable, "R." (Table 1)

**Table 1. Holding Time Criteria**

Matrix	Preserved	Criteria	Action	
			Detected compounds	Non-detected compounds
Aqueous	No	≤ 7 days(extraction) ≤ 40 days(analysis)	Use professional judgement	
	No	> 7 days(extraction) > 14 days(analysis)	Use professional judgement	
	Yes	≤ 7 days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 7 days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	Grossly exceeded	J	UJ or R
Non-aqueous	No	≤ 14days(extraction) ≤ 40 days (analysis)	Use professional judgement	
	No	> 14days(extraction) >40 days(analysis)	Use professional judgement	
	Yes	≤ 14days(extraction) ≤ 40 days(analysis)	No qualification	
	Yes	> 14days(extraction) > 40 days(analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R

9.0 Surrogate Recovery (Form II)

9.1 The analyst must monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

9.2 Were the recoveries of the surrogate spikes presented on CLP Surrogate Recovery Summary forms (Form II), or equivalent, for each of the following matrices?

- a. Water/Waste
- b. Soil/Solid

ACTION: Call lab for explanation/resubmittals. If missing deliverables or information are unavailable, document the effect in the data assessment.

9.3 Are all the pesticide samples listed on the appropriate surrogate recovery form for each of the following matrices?

- a. Water
- b. Waste
- c. Soil/Solid

9.4 The laboratory must evaluate the surrogate data from individual samples versus the surrogate control limits developed by the laboratory. Method 8000C, Sec 9.0 details evaluating surrogate data and updating surrogate limits. If laboratory established recovery limits are not established, use surrogate recovery between 70 - 130% for all samples, including MS, MSDs, LCSs, and all blanks. Are surrogate recovery limits met?

ACTION: Circle all outliers in red. Follow surrogate action Table 2.

9.5 Were surrogate retention times (RT) within the windows established during the initial 5-point analysis?

ACTION: Follow surrogate action, Table 2 below.

**Table 2. Surrogate Recovery Criteria**

Criteria	Action	
	Detected Target Compounds	Non-detected Target Compounds
%R > 200%	J	Use professional judgement
130% < %R ≤ 200%	J	No qualification
70% ≤ %R ≤ 130%	No qualification	
10% ≤ %R < 70%	J	UJ
%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	Use professional judgement	
RT out of RT window	Use professional judgement	
RT within RT window	No qualification	

9.6 Are there any transcription/calculation errors between raw data and Form II?

ACTION: If large errors exist, call lab for explanation/resubmittal. Make any necessary corrections and document the effect in data assessments.

10.0 Laboratory Control Sample

10.1 Is the LCS prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per SDG.

**ACTION:** If any Laboratory Control Sample data are missing, call the lab for explanation/ resubmittals. Make note in the data assessment.

10.2 Are raw data and percent recoveries present for all Laboratory Control samples as required by Method 8000C (section 9.5).

Verify that QC check samples were extracted and analyzed by the same procedures used for the actual samples.

**ACTION:** If any Laboratory Control Sample data are missing, call the lab for explanation/ resubmittals. Make note in the data assessment.

**Note:** When the results for matrix spike analysis indicates a problem due to sample matrix effects, the LCS results are used to verify the laboratory can perform the analysis in a clean sample.

10.3 Were the Laboratory Control Samples analyzed for all the nitroaromatics and nitroamines analytes that the samples are analyzed for.

10.4 Were Laboratory Control Samples analyzed at the required concentration as specified in Method 8000C(sec 9.5)(near the middle of the calibration range) for all target analytes.

**ACTION:** If Laboratory Control Samples were not analyzed at the required concentration or the required frequency, make note in the data assessment and use professional judgement to determined the affect on the data.

10.5 Did laboratory calculate in-house performance criteria for LCS recoveries according to Method 8000C section 9.7, and were recoveries met?

10.6 If in house LCS recoveries performance criteria were not generated, the laboratory should use 70 - 130% criteria, and was this criteria met?

10.7 If LCS recovery criteria were not met, were Laboratory Control Samples re-analyzed?

**ACTION:** If QC check samples were not re-analyzed, or a general system problem is indicated by repeated failure to meet the QC acceptance criteria specified in the method, make note in the data assessment and use Table 3 recovery actions criteria.

**Table 3. LCS Recovery Actions**

Criteria	Action	
	Detected Associated Compounds	Non-Detected Compounds
%R > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	R
Lower Acceptance Limit $\leq$ %R $\leq$ Upper Acceptance Limit	No qualifications	

11.0 Matrix Spikes (Form III)

11.1 Are all data for one matrix spike and matrix duplicate (unspiked) pair (MS/Dup) or matrix spike/matrix spike duplicate (MS/MSD) present and complete for each matrix.

**NOTE:** For soil and waste samples showing detectable amounts of organics, the lab may substitute replicate samples in place of the matrix spike.

11.2 Have MS/Dup or MS/MSD results been summarized on modified CLP Form III?

**ACTION:** If any data are missing take action as specified in section 3.2 above.

11.3 Were matrix spikes analyzed at the required frequency for each of the following matrices? (One MS/Dup, MS/MSD must be performed for every 20 samples of similar matrix or concentration level.

- a. Water
- b. Waste
- c. Soil/Solid

**ACTION:** If any MS/Dup or MS/MSD data are missing, take the action specified in 3.2 above.

11.4 Were the Matrix Spike Samples spiked and analyzed for all the nitroaromatics and nitroamines analytes that the samples are analyzed for (Same analytes as LCS).

ACTION: If no, did the lab use the optional QC acceptance criteria discussed in Method 8000C(section 9.7)?

List the criteria used and make note in data assessment.

Criteria used \_\_\_\_\_

11.5 Were Laboratory Control Samples analyzed at the required concentration as specified in Method 8000C(sec (9.5)(Same concentration as LCS) for all target analytes.

\_\_\_\_\_

11.6 Did laboratory calculate in-house performance criteria for matrix spike recoveries according to Method 8000C section 9.7, and were recoveries met?

\_\_\_\_\_

11.7 If in house LCS recoveries performance criteria were not generated, the laboratory should use 70 - 130% criteria, and was this criteria met?

\_\_\_\_\_

11.8 How many matrix spike recoveries are outside the in-house performance criteria or QC limits of 70 - 130%?

Water  
\_\_\_\_ out of \_\_\_\_

Soil  
\_\_\_\_ out of \_\_\_\_

11.9 How many RPDs for the Matrix Spike and Matrix Spike Duplicate (if applicable) recoveries are greater than the QC limit of 20%?

Water  
\_\_\_\_ out of \_\_\_\_

Soil  
\_\_\_\_ out of \_\_\_\_

11.8 Were the matrix spike and matrix spike duplicate recovery and RPD limits met as specified in Table 4. Note: No qualification of the data is necessary on MS and MSD data alone. Use professional judgement to use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. If any MS and MSD, percent recovery, or RPD results in the nitroaromatics and nitroamines fraction is out of specification (Table 4), use professional judgement to qualify data to include the consideration of the existence interference in the raw data. In some instances it may be determined that only the replicate or spiked samples are affected. Alternatively, the data may suggest that the laboratory is having a systematic problem with one or more analytes, thereby affecting all associated samples. Use professional judgement to determine the need for qualification of detects of non-spiked compounds.

**Table 4. MS/MSD Actions for Analysis**

Criteria	Action	
	Detected Associated Compounds	Non-Detected Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgement
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualifications	

12.0 Blanks (Form IV)

12.1 Was reagent blank data reported on CLP equivalent Method Blank Summary form(s) (Form IV)?  \_\_\_ \_\_\_

12.2 Frequency of Analysis: Has a reagent blank been analyzed for every 20 (or less) samples of similar matrix or concentration or each extraction batch?  \_\_\_ \_\_\_

**ACTION:** If any blank data are missing, take action as specified above (section 3.2). If blank data is not available, reject (R) all associated positive data. However, using professional judgement, the data reviewer may substitute field blank data for missing method blank data.

12.3 Chromatography: review the blank raw data - chromatograms, quant reports or data system printouts.

Is the chromatographic performance (baseline stability) for each instrument acceptable for nitroaromatics and nitramines?  \_\_\_ \_\_\_

13.0 Contamination



NOTE: "Water blanks", "distilled water blanks" and "drilling water blanks" are validated like any other sample and are not used to qualify the data. Do not confuse them with the other QC blanks discussed below.

13.1 Do any method/instrument/reagent/cleanup blanks have positive results for nitroaromatics or nitramines? When applied as described below, the contaminant concentration in these blanks are multiplied by the sample Dilution Factor and corrected for % moisture when necessary.

\_\_\_ [ ] \_\_\_

13.2 Do any field/rinse blanks have positive nitroaromatics or nitramines results?

\_\_\_ [ ] \_\_\_

ACTION: Prepare a list of the samples associated with each of the contaminated blanks. (Attach a separate sheet.)

NOTE: All field blank results associated to a particular group of samples (may exceed one per case or one per day) may be used to qualify data. Blanks may not be qualified because of contamination in another blank. Field blanks must be qualified for surrogate, or calibration QC problems.

ACTION: Follow the directions in Table 5 below to qualify sample results due to contamination. Use the largest value from all the associated blanks.

**Table 5. Blank Contamination Criteria**

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Blank Type	Blank Result	Sample Result	Action for Samples
Method, Clean up, Instrument, Field	Detects	Not detected	No qualification
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgement
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank contamination	Report the concentration for the sample with a U, or quantify the data as unusable R
		≥ CRQL and ≥ blank contamination	Use professional judgement
	= CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgement
	Gross contamination	Detects	Qualify results as unusable R

NOTE: If gross blank contamination exists(e.g., saturated peaks, “hump-o-grams,” “junk” peaks), all affected positive compounds in the associated samples should be qualified as unusable “R”, due to interference. Non-detected pesticide target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

13.3 Are there field/rinse/equipment blanks associated with every sample?

ACTION: For low level samples, note in data assessment that there is no associated field/rinse/ equipment blank. Exception: samples taken from a drinking water tap do not have associated field blanks.

14.0 HPLC Apparatus and Materials

14.1 Was the proper HPLC chromatographic column used for the analysis of nitroaromatics or nitramines?

Action: Check raw data, instrument logs, or contact the lab to determine what type of columns were used. (Method 8330A, section 4.1)

14.2 Indicate the specific type of HPLC column.

column 1: \_\_\_\_\_

column 2: \_\_\_\_\_

ACTION: Note any changes to the suggested materials in section 14.1 above in the data assessment. Also note the impact (positive or negative) such changes have on the analytical results.

#### 15.0 Calibration and HPLC Performance

15.1 Are the following liquid chromatograms and data systems printouts for both columns present for all samples, blanks, MS, replicates?

- |  |                          |                          |                          |
|--|--------------------------|--------------------------|--------------------------|
| a. Samples                             | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| b. All blanks                          | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| c. Matrix spike samples                | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| d. 5 pt. initial calibration standards | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| e. Calibration verification standards  | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| f. Laboratory Control samples (LCS)    | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

ACTION: If no, take action specified in 3.2 above.

15.2 Are data summary forms (containing calibration factors or response factors) for the initial 5 pt. calibration and daily calibration verification standards present and complete for each column and each analytical sequence?

NOTE: External standard calibration procedures are used (Method 8000C (section 11.4.2), therefore calibration factors must be used.

ACTION: If any data are missing or it cannot be determined how the laboratory calculated calibration factors, contact the lab for explanation/resubmittals. Make necessary corrections and note any problems in the data assessment.

15.3 Are there any transcription/calculation errors between raw data and data summary forms?

\_\_\_  \_\_\_

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and document the effect in data assessments.

15.4 Are standard retention time (RT) windows for each nitroaromatics and nitramines peak of interest presented on modified CLP summary forms?

\_\_\_ \_\_\_

ACTION: If any data are missing, or it cannot be determined how RT windows were calculated, call the lab for explanation/resubmittals. Note any problems in the data assessment.

NOTE: Retention time windows for all nitroaromatics and nitramines are established using retention times from three calibration standards analyzed during the entire analytical sequence (Method 8000C section 11.6).

Best results are obtained using retention times which span the entire sequence; i.e., using the calibration verification/continuing calibration standards analyzed every 12 hours.

15.5 Were RT windows on the confirmation column established using three standards as described above?

\_\_\_ \_\_\_

NOTE: RT windows for the confirmation column should be established using a 3 pt. calibration, preferably spanning the entire analytical sequence as described in 15.4 above. If RT windows on one column are tighter than the other, this may result in false negatives when attempting to identify compounds in the samples.

ACTION: Note potential problems, if any, in the data assessment.

15.6 Do all standard retention times in each level of the initial 5 pt. calibrations for nitroaromatics and nitramines fall within the windows established during the initial calibration sequence?

\_\_\_ \_\_\_

ACTION i: If no, all samples in the entire analytical sequence are potentially affected. Check to see if three standards spanning the entire sequence were used to obtain RT windows. If the lab used three standards from the 5 pt., RT windows may be too tight. If so, RT windows should be recalculated as per Method 8000C (section 11.6).

ii. Alternatively, check to see if the chromatograms contain peaks within an expanded window surrounding the expected retention times.

If no peaks are found and the surrogates are visible, non-detects are valid.  
 If peaks are present but cannot be discerned through pattern recognition  
 or by using revised RT windows, qualify all positive results and  
 non-detects as unusable, "R".

15.7 Has the linearity criteria for the initial calibration standards been satisfied for both columns?  
 (% RSD for the calibration factors (CFs) must be < 20.0% for all analytes).

ACTION: If no, follow Table 6 criteria.

**Table 6. Initial Calibration CF Action for Nitroaromatic and Nitramine Analysis**

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
% RSD > 20%	J	UJ
% RSD within allowable limits	No qualifications	

15.8 Does the calibration verification/continuing calibration standard contain the nitroaromatics or nitramines peaks of interest, analyzed on each working day, prior to sample analyses?

15.9 Has a calibration verification/continuing calibration standard been analyzed after every 10 samples and at the end of each analytical sequence

ACTION: If no, take action as specified in section 3.2 above.

15.10 Has the percent difference (%D) between the Calibration Factor (CF) of the peaks used to identify the nitroaromatics and nitramines in the CCV and the CF from these peaks in the initial calibration exceeded  $\pm 15\%$ .

15.11 Has a new 5 pt. initial calibration curve been generated for those nitroaromatics and nitramines analytes which failed in the calibration verification/continuing calibration

standard (8000C, section 11.7.3), and all samples which followed the out-of-control calibration verification/standard continuing calibration standard?

**ACTION:** If the %D for any analyte exceeded the  $\pm 15\%$  criterion and the instrument was not recalibrated for those analytes, qualify positive results for all associated samples (those which followed the out-of-control standard) "J" and sample quantitation limits "UJ". (Table 7)

15.12 Have retention time (RT) windows been properly calculated for each analyte of interest (Method 8000C, section 11.6), using RTs from the associated calibration verification/continuing standard?

**ACTION:** If no, take action specified in section 3.2 above

15.13 Do all standard retention times for each calibration verification/continuing calibration standard fall within the windows established during the initial calibration sequence?

15.14 Do all standard retention times for each mid-concentration standard (analyzed after every 10 samples) fall within the daily RT windows.

**ACTION:** If the answer to either 15.12 or 15.13 above is no, check the chromatograms of all samples which followed the last in-control standard. All samples analyzed after the last in-control standard must be re-injected, if initial analysis indicated the presence of the specific analyte that exceeded the retention time criteria). If samples were not re-analyzed, document under Contract Non-compliance in the Data Assessment.

Reviewer has two options to determine how to qualify questionable sample data. First option is to determine if possible peaks are present within daily retention time window. If no possible peaks are found, non-detects are valid. If possible peaks are found (or interference), qualify positive hits as presumptively present "NJ" and non-detects are rejected "R". Second option is to use the ratio of the retention time of the analyte over the retention time of either surrogate. The passing criteria is  $\pm 0.06$  RRT units of the RRT of the standard component. Reject "R" all questionable analytes exceeding criteria, and "NJ" all other positive hits.

15.15 Has no more than 14 hours elapsed from the injection of the opening CCV and the end of the analytical sequence (closing CCV). (Table 7)

**Table 7. CCV Criteria**

Criteria	Action	
	Detected Associated	Non-Detected Associated

	Compounds	Compounds
RT out of RT window	Use professional judgement (Sec 15.14)	
%D not within +/- 15%	J	UJ
Time elapsed greater than section 15.15 criteria.	R	
%D, time elapsed, RT are all within acceptable limits.	No qualifications	

15.16 Are there any transcription/calculation errors between raw data and data summary forms?

**ACTION:** If large errors exist call lab for explanation/resubmittal, make any necessary corrections and document the effect in data assessments under "Conclusions".

16.0 Analytical Sequence Check (Form VIII-nitroaromatics and nitramines)

16.1 Have all samples been listed on CLP Form VIII or equivalent, and are separate forms present for each column?

**ACTION:** If no, take action specified in 3.2 above.

16.2 Was the proper analytical sequence followed for each initial calibration and subsequent analyses?

**Note:** Sequence is as follows: 5 point initial calibration, method blank, LCS, CCS, 10 sample extracts, CCV, 10 sample extract, and so on. The sequence must always end with a CCV. As long as the first CCV is within QC, the initial calibration does not have to be rerun.

**ACTION:** If no, use professional judgement to determine the severity of the effect on the data and qualify it accordingly. Generally, the effect is negligible unless the sequence was grossly altered or the calibration was also out of limits.

16.3 Were the surrogate RTs for the samples within the mean surrogate RT from the initial calibration?

**Action:** If no, see "Action" in section 15.14 above

17.0 Extraction Techniques for Sample Preparation

Method 8330A permits a variety of extraction techniques to be used for sample preparation. Which extraction procedure was used?

17.1 Aqueous samples:

- 1. Low Level (salting-out extraction)
- 2. High-level (Sample filtration)
- 3. Solid phase extraction (Method 3535)
- 4. Other

17.2 Soil and sediment samples:

- 1. Sonication
- 2. Other

18.0 Nitroaromatics and Nitramines Identification

18.1 Has CLP Form X or equivalent, showing retention time data for positive results on the two HPLC columns, been completed for every sample in which a nitroaromatics or nitramines was detected?

ACTION: If no, take action specified in 3.2 above, or compile a list comparing the retention times for all sample hits on the two columns.

18.2 Are there any transcription/calculation errors between raw data and data summary forms (initial calibration summaries, calibration verification summaries, analytical sequence summaries).

ACTION: If large errors exist, call lab for explanation/resubmittal, make necessary corrections and note error in the data assessment.

18.3 Are retention times (RT) of sample compounds within the established RT windows for both columns/analyses?

ACTION: Qualify as unusable (R) all positive results which were not confirmed by second HPLC column analysis. Also qualify "R", unusable, all positive results not within RT windows unless associated standard compounds are similarly biased. The reviewer should use professional judgement to assign an appropriate quantitation limit.



18.4 Check chromatograms for false negatives, especially if RT windows on each column were established differently. Were there any false negatives? \_\_\_\_\_ [ ] \_\_\_\_\_

**ACTION:** Use professional judgement to decide if the compound should be reported. If there is reason to believe that peaks outside retention RT windows should be reported, make corrections to data summary forms (Form I) and note in data assessment.

18.5 Is the percent difference (%D) calculated for the positive sample results on the two HPLC columns < 25.0%? \_\_\_\_\_ [ ] \_\_\_\_\_

**NOTE:** The method requires quantitation from one column. The second column is to confirm the presence of an analyte. It is the reviewer's responsibility to verify from the project plan what the lab was required to report. If the lab was required to report concentrations from both columns, continue with validation for % Difference. If required, but not reported, either contact the lab for results or calculate the concentrations from the calibration. If not required, skip this section. Document actions in Data Assessment.

**ACTION:** If the reviewer finds neither column shows interference for the positive hits, the data should be qualified as follows:

<u>% Difference</u>	<u>Qualifier</u>
0-25%	none
26-70%	"J"
71-100%	"NJ"
101-200% (No Interference)	"R"
101-200% (Interference detected)**	"NJ"
>50% (Analyte value is <CRQL)	"U"
>200%	"R"

**Note:** The lower of the two values is reported on Form I. If using professional judgement, the reviewer determines that the higher result was more acceptable, the reviewer should replace the value and indicate the reason for the change in the data assessment.

## 19.0 Compound Quantitation and Reported Detection Limits

19.1 Are there any transcription/calculation errors in Form I results? Check at least two positive values. Were any errors found? \_\_\_\_\_ [ ] \_\_\_\_\_

NOTE: Nitroaromatics and Nitramines peak results can be checked for rough agreement between quantitative results obtained on the two HPLC columns. The reviewer should use professional judgement to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interference is suspected, the lower of the two values should be reported and qualified according to section 18.5 above. This necessitates a determination of an estimated concentration on the confirmation column. The narrative should indicate that the presence of interferences has led to the quantitation of the second column confirmation results.

19.2 Are the EDLs (Estimated Detection Limits) adjusted to reflect sample dilutions and, for soils, % moisture?

ACTION: If errors are large, call lab for explanation/resubmittal, make any necessary corrections and document effect in data assessments.

ACTION: When a sample is analyzed at more than one dilution, the lowest EDLs are used (unless a QC exceedance dictates the use of the higher EDL data from the diluted sample analysis). Replace concentrations that exceed the calibration range in the original analysis by crossing out the value on the original Form I and substituting it with data from the analysis of diluted sample. Specify which Form I is to be used, then draw a red "X" across the entire page of all Form I's that should not be used, including any in the summary package.

ACTION: EDLs affected by large, off-scale peaks should be qualified as unusable, "R". If the interference is on-scale, the reviewer can provide a modified EDL flagged "UJ" for each affected compound.

#### 14.0 Chromatogram Quality

14.1 Were baselines stable?

14.2 Were any electropositive displacement (negative peaks) or unusual peaks seen?

ACTION: Note all system performance problems in the data assessment.

#### 15.0 Field Duplicates

15.1 Were any field duplicates submitted for Nitroaromatics and Nitramines.

**ACTION:** Compare the reported results for field duplicates and calculate the relative percent difference.

**ACTION:** Any gross variation between field duplicate results must be addressed in the reviewer narrative. However, if large differences exist, the identity of the field duplicates is questionable. An attempt should be made to determine the proper identification of field duplicates.